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# A new ultra-violet band-system of GeCl

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With 1 plate

## Abstract

The vibrational analysis of a new band-system of GeCl is reported. The upper state is probably ${}^2\Delta$, and the lower state is the ${}^2\Pi$ ground state of GeCl. The constants derived are as follows:

| $\nu_e$ | $\omega_e$ | $x_e\omega_e$ |
|---|---|---|
| 29561.7 | 335.5 | 4.58 cm$^{-1}$ |
| 29499.8 | 342.1 | 4.65 |
| 975.0 | 405.5 | 1.23 |
| 0 | 407.6 | 1.36 |

Similarities between the spectra of GeCl and SnCl are noted.

## 1. Introduction

Preliminary observations of the spectrum emitted by germanium tetrachloride vapour excited by active nitrogen showed two sequences of bands degraded to the red with the strongest heads at 3393 and 3501 A. The energy-difference between these corresponds approximately to that found by JEVONS, BASHFORD and BRISCOE for the ${}^2\Pi_{3/2} - {}^2\Pi_{1/2}$ separation in GeCl from their analysis of the ultra-violet system, ${}^2\Sigma \rightarrow {}^2\Pi$.[1] This latter system was also developed rather strongly in active nitrogen, and it therefore seemed likely that the new sequences formed a second ultra-violet transition of GeCl, perhaps analogous to the ${}^2\Delta \rightarrow {}^2\Pi$ system of SnCl.[2] More intense sources were therefore investigated. A Tesla discharge through a stream of germanium tetrachloride gave a pure, but rather feeble, spectrum, and ultimately a positive-column discharge through flowing germanium tetrachloride vapour was adopted.

A conventional silica discharge-tube about 35 cm long, 1 cm diameter, with molybdenum rod electrodes some 20 cm apart, was used. The final plates were taken on Ilford Process plates in a first order of a 2.4-m grating instrument giving a linear dispersion of about 7.4-A/mm. Exposure times, with about 500-v across the tube, and a current of about 0.1 amp, were about 20 minutes.

The band-heads were measured by us independently against internal standards lines of Ge and Mo whose wavelengths were taken from the M. I. T. list[3]: means of the two sets of measurements were then taken.

The vibrational analysis of the bands shows that they are indeed to be ascribed to a transition, probably $^2\Delta \rightarrow {}^2\Pi$, in which the lower state is the already-known $^2\Pi$ ground state of GeCl. This identification was further confirmed through the kindness of Dr JEVONS, who lent us the plates taken for the analysis of the $^2\Sigma \rightarrow {}^2\Pi$ system in 1937. These plates also showed the 3393 and 3501 sequences, though somewhat less clearly, probably because of the somewhat higher current-densities used by JEVONS, BASHFORD and BRISCOE.

## 2. Vibrational analysis

A reproduction of part of a spectrogram is given in Plate 1. There are seen to be two strong sequences: we take the heads at 3393 A to be those of the 0, 0 transition going to $^2\Pi_{1/2}$, and those at 3501 A to be those of the 0, 0 transition going to $^2\Pi_{3/2}$ (assuming that the ground state is regular). The shorter wavelength system will be called sub-system I, the longer wavelength system sub-system II.

**Sub–system I.** Measurements of the band-heads are given in Table 1 and a Deslandres array is set out in Table 2. Of the features whose identification or interpretation is doubtful, only those which have been measured independently by us both are included in Table 1.

*Table 1.*

Band-head data for sub-system I.

| $\lambda_{\text{air}}$ | $\nu_{\text{vac}}$ | Intensity | $v', v''$ | $\lambda_{\text{air}}$ | $\nu_{\text{vac}}$ | Intensity | $v', v''$ |
|---|---|---|---|---|---|---|---|
| $3354.5_2$ | $29802._0$ | 0 ? | 1, 0 | 3401.08 | 29394.0 | 5 | 1, 1 |
| 58.12 | 770.0 | 0 ? | ? | 09.86 | 318.3 | 1 | 2, 2 V |
| 63.67 | 720.9 | 0 | 2, 1 | 10.33 | 314.3 | 3 | 2, 2 |
| 65.1 | 708 | 0 ? | ? | 20.09 | 230.6 | 2 | 3, 3 |
| 69.68 | 667.9 | 0 ? | ? | 31.37 | 134.6 | 1 | 4, 4 |
| 70.78 | 658.2 | 0 ? | ? | 36.86 | 088.0 | 1 | ? |
| $74.2_0$ | $628._2$ | 0 | 3, 2 | 38.83 | 071.4 | 1 | 0, 1 V |
| 84.63 | 536.9 | 1 | 4, 3 | 39.99 | 061.5 | 2 | 0, 1 |
| $86.0_8$ | $524._2$ | 3 L | ? | 47.25 | 000.2 | 1 | 1, 2 V |
| 87.86 | 508.7 | 3 L | ? | 47.94 | 28994.6 | 2 | 1, 2 |
| 89.77 | 492.1 | 1 L | ? | $57.3_1$ | $916._0$ | 1 | 2, 3 |
| 90.32 | 487.3 | 1 L | ? | 67.52 | 830.8 | 1 | 3, 4 |
| 92.07 | 472.1 | 5 | 0, 0 V | $70.8_0$ | $803._6$ | 1 | ? |
| 92.74 | 466.3 | 9 | 0, 0 | $78.8_8$ | $736._6$ | 0 | 4, 5 |
| 94.94 | 447.2 | 1 | ? | $87.7_5$ | $663._6$ | 0 | 0, 2 |
| 3400.48 | 399.2 | 3 | 1, 1 V | $96.3_9$ | $592._8$ | 1 | 1, 3 |

L . . . line-like.

The bands have at least two heads of comparable intensity, and their structure is further complicated by the isotope effect to which contributions are made both by chlorine and by germanium[1]. It is, however, believed that the measurements included in the Deslandres scheme are of the stronger, longer wavelength, Q-like heads of the most abundant molecule, $^{74}\text{Ge}\,^{35}\text{Cl}$.

*Table 2.*

GeCl : Sub-system I.

| | | | | | | |
|---|---|---|---|---|---|---|
| 4 | | | | 29536.9 402.3<br>306.3 | 29134.6 398.$_0$<br>303.8 | 28736.$_6$ |
| 3 | | | 29628.$_2$ 397.$_4$<br>313.$_9$ | 29230.6 399.8<br>314.$_6$ | 28830.8 | |
| 2 | | 29720.9 406.6<br>326.9 | 29314.3 398.$_3$<br>319.7 | 28916.$_0$<br>323.$_2$ | | |
| 1 | 29802.$_0$ 408.$_0$<br>335.$_7$ | 29394.0 399.4<br>332.$_5$ | 28994.6 401.$_8$<br>331.$_0$ | 28592.$_8$ | | |
| 0 ↑ | 29466.3 404.8 | 29061.5 397.$_9$ | 28663.$_6$ | | | |
| $v'$ / $v''$ → | 0 | 1 | 2 | 3 | 4 | 5 |

The most clearly-observed subsidiary heads — not arising from isotope effect — are indicated in table 1 by »V». The separation of the V from the main heads is not constant from band to band, but varies with the transition in the manner to be expected for a head-origin separation where B′ changes more rapidly with vibrational quantum number than B″ (as may be expected here, since, as will be seen, $x_e' > x_e''$): thus the separation decreases from 5.8 cm$^{-1}$ for the 0, 0 band to about 4.0 cm$^{-1}$ for the 2, 2 band.

However, although the 0, 0 band of sub-system I has at first sight only a relatively simple double-headed structure, attention should be drawn to the weaker subsidiary features listed in table 1 between 3386 and 3390.5 A. Some of these may be heads formed by satellite branches in the 0, 0 transition.

**Sub-system II.** The bands of sub-system II (Table 3) present immediately a much more complex appearance even than those of I. In the region of the 0, 0 band, for example, there are no less than three strong heads, at 28560.8 (7), 28551.0 (10), and 28514.9 (8), a weaker head at 28554.5 (4) and a diffuse minimum of intensity at 28538.0 cm$^{-1}$. Somewhat similar features are probably shown by the other bands — though less clearly on account of the complicated vibrational isotope pattern.

We have again taken the strongest heads to form the Deslandres scheme in Table 4, and it will be seen that the vibrational intervals agree tolerably well with those from I. We have therefore little doubt as to the essential correctness of the analysis, but it is nevertheless found that even when account is taken of the inherent double-headedness of the bands and of the isotope effect, a number of bands — some of considerable strength — remain unexplained. The majority of these heads, marked III in Table 3, fit together into a vibrational scheme with 28514.9 as the 0, 0 head, and with constants given approximately by the following equation:

$$\nu_h\,(\mathrm{III}) = 28549 + 332\,(v' + \tfrac{1}{2}) - 4.0\,(v' + \tfrac{1}{2})^2 - 401\,(v'' + \tfrac{1}{2}) + 0.6\,(v'' + \tfrac{1}{2})^2.$$

The vibrational constants are so close to those deduced for the main heads of the two sub-systems (see later) that it seems certain that the heads III belong to the same electronic transition. It is difficult, however, to decide whether they arise from satellite branches, or from the fortuitous piling-up of rotational structure, as, for example, happens for BBr[4].

*Table 3.*

Band-head data for sub-system II.

| $\lambda_{\text{air}}$ | $\nu_{\text{vac}}$ | Intensity | $v', v''$ | $\lambda_{\text{air}}$ | $\nu_{\text{vac}}$ | Intensity | $v', v''$ |
|---|---|---|---|---|---|---|---|
| $3461.4_0$ | $28881._8$ | 0 | 1, 0 | $3565.0_9$ | $28041._8$ | 0 | III |
| 72.09 | 792.9 | 1 | 2, 1 | $69.3_9$ | $008._0$ | 1 | ? |
| 77.2 | 751 | 0 | III | $69.6_7$ | $005._8$ | 1 | 2, 3? i |
| 83.24 | 700.7 | 2 | 3, 2 | $70.5_1$ | $27999._2$ | 2 | 2, 3? |
| 87.81 | 663.1 | 0 | 0, 2 I or III | 71.03 | 995.2 | 4 | 2, 3 |
| 95.29 | 601.8 | 2 | 4, 3 | 75.92 | 956.9 | 1 | III |
| 99.18 | 570.0 | 0 | III | 80.43 | 921.7 | 2 | 3, 4? i |
| 3500.31 | 560.8 | 7 | 0, 0 V | 81.97 | 909.7 | 3 | 3, 4 |
| 01.08 | 554.5 | 4 | 0, 0 | $87.5_0$ | $866._6$ | 2 | III |
| 01.51 | 551.0 | 10 | 0, 0 | 92.41 | 828.6 | 1 | 4, 5? i |
| 03.10 | 538.0 | gap | 0, 0 | 94.30 | 813.9 | 3 | 4, 5 |
| $03.5_8$ | $534._1$ | 4? | 0, 0 | $99.9_1$ | $770._6$ | 0 | III |
| 05.94 | 514.9 | 8 | III | 3605.02 | 731.2 | 1 | 5, 6? i |
| 07.70 | 500.6 | 4 | 5, 4 | 06.82 | 717.4 | 1 | 5, 6 or III |
| 08.48 | 494.3 | 1 | 5, 4? | 08.37 | 705.5 | 1 | ? |
| $08.9_0$ | $490._8$ | 1? | ? | 11.47 | 681.7 | 1 | 1, 3 |
| 10.34 | 479.2 | 7 | 1, 1 V | $16.9_1$ | $640._0$ | 0 | III |
| 10.99 | 473.9 | 9 | 1, 1 | 18.96 | 624.4 | 1 | ? |
| 11.94 | 466.2 | gap | 1, 1 | 21.81 | 602.7 | 2 | 2, 4 |
| $12.5_9$ | $460._9$ | 3? | ? | $30.3_5$ | $537._7$ | 1 | 3, 5? i |
| 15.38 | 438.3 | 5 | III | 33.13 | 516.7 | 4 | 3, 5 |
| $16.8_3$ | $426._6$ | 2 | ? | 42.66 | 444.7 | 1 | 4, 6? i |
| 21.06 | 392.4 | 7 | 2, 2 | 45.41 | 424.0 | 3 | 4, 6 |
| 25.72 | 354.9 | 2 | III | 46.17 | 418.3 | 1 | 4, 6? i |
| 31.50 | 308.5 | 1 | 3, 3? i | 47.01 | 411.9 | 1 | 4, 6? i |
| 32.21 | 302.8 | 5 | 3, 3 | 58.98 | 322.3 | 3 | 5, 7 |
| 37.07 | 263.9 | 1 | III | 74.77 | 204.9 | 1 | 2, 5 |
| $40.5_6$ | $236._1$ | 1? | ? | 75.73 | 197.8 | 1 | 2, 5? i |
| 43.45 | 213.0 | 0 | 4, 4? i | $85.4_1$ | $126._3$ | 1 | 3, 6 |
| 44.33 | 206.2 | 2 | 4, 4 | $97.6_6$ | $036._5$ | 2 | 4, 7 |
| 49.29 | 166.6 | 1 | III | $98.7_5$ | $028._5$ | 1 | 4, 7? i |
| 51.17 | 151.7 | 4 | 0, 1 | $99.7_0$ | $021._6$ | 1 | 4, 7? i |
| $55.1_6$ | $120._1$ | 2 | 5, 5? i | $3711.4_3$ | $26936._2$ | 1 | 5, 8 |
| 55.95 | 113.9 | 3 | 5, 5 or III | $12.4_3$ | $928._9$ | 0 | 5, 8? i |
| 59.72 | 084.1 | 3 | 1, 2? V or i | $13.6_4$ | $920._1$ | 0 | 5, 8? i |
| 60.81 | 075.5 | 4 | 1, 2 | $15.7_4$ | $904._9$ | 0 | ? |

? i . . . possible isotope head.

## *Table 4.*

### GeCl : Sub-system II.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5 | | | | | 28500.6 386.1<br>294.4 | 28113.9 396.5<br>290.0 | 27717.4 395.1<br>293.4 | 27322.3 386.$_1$<br>285.$_8$ | 26936.$_2$ |
| 4 | | | | 28601.8 395.6<br>299.0 | 28206.2 392.3<br>296.5 | 27813.9 389.9<br>297.2 | 27424.0 387.$_5$<br>297.$_7$ | 27036.$_5$ | |
| 3 | | | 28700.7 397.9<br>308.3 | 28302.8 393.1<br>307.6 | 27909.7 393.0<br>307.0 | 27516.7 390.$_4$<br>311.8 | 27126.$_3$ | | |
| 2 | | 28792.9 400.5<br>319.0 | 28392.4 397.2<br>316.9 | 27995.2 392.5<br>313.5 | 27602.7 397.8 | 27204.9 | | | |
| 1 | 28881.$_8$ 407.$_9$<br>330.$_8$ | 28473.9 398.4<br>322.2 | 28075.5 393.8 | 27681.7 | | | | | |
| 0 | 28551.0 399.3 | 28151.7 | | | | | | | |
| $\uparrow$ $v'$ / $v'' \to$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |

**The $^2\Sigma \rightarrow {}^2\Pi$ system.** There appeared to be less overlapping of bands on our plates of this system than on those taken by JEVONS, BASHFORD and BRISCOE — presumably because of a lower rotational temperature following from our reduced current-density — and as a result we were able to measure a few additional bands of this system. The data are given in Table 5.

*Table 5.*

New band-heads in the $^2\Sigma \rightarrow {}^2\Pi$ system.

| $\lambda_{\text{air}}$ | $\nu_{\text{vac}}$ | $v', v''$ | Sub-system |
|---|---|---|---|
| 2914.98 | 34295.5 | 2, 2 | ii |
| 95.76 | 33373.0 | 1, 3 | ii |
| 3030.89 | 32984.0 | 1, 4 | ii |
| 80.63 | 451.5 | 0, 4 | ii |
| 85.66 | 398.6 | 1, 3 | i |
| 3149.70 | 31739.9 | 2, 6 | i |
| 3216.19 | 083.7 | 0, 5 | i |

## 3. Results

**The vibrational constants for the lower state.** The values of $\Delta G''_{v,v+1}$ derived both from the $^2\Sigma \rightarrow {}^2\Pi$ and the new system are given in Table 6. The agreement between the sets of values for the two systems is strong evidence that the same lower state is involved in both. Since there appears to be a small systematic difference between the vibrational intervals for the two sub-states, the constants were evaluated separately, using all the figures available, and weighting intervals simply in proportion to the number of observations.

*Table 6.*

Values of $\Delta G''_{v,v+1}$.

| $v, v+1$ | $^2\Pi_{1/2}$ (a) | $^2\Pi_{1/2}$ (b) | $^2\Pi_{3/2}$ (a) | $^2\Pi_{3/2}$ (b) |
|---|---|---|---|---|
| 0, 1 | 405.6 | 406.4 | 404.8 | 403.6 |
| 1, 2 | 400.4 | 401.2 | 402.4 | 399.5 |
| 2, 3 | 397.2 | 399.0 | 399.0 | 396.3 |
| 3, 4 | 89.0 | 401.1 | 97.6 | 93.7 |
| 4, 5 | | 398.1 | 89.4 | 92.3 |
| 5, 6 | 89.1 | | | 92.3 |
| 6, 7 | | | | 91.3 |
| 7, 8 | | | | 86.1 |

(a) from $^2\Sigma \rightarrow {}^2\Pi$ system,
(b) from new system.

The results are: For $\Pi_{1/2}$, $G'' = 407._6\,(v+\frac{1}{2}) - 1.3_6\,(v+\frac{1}{2})^2$,
For $\Pi_{3/2}$, $G'' = 405._5\,(v+\frac{1}{2}) - 1.2_3\,(v+\frac{1}{2})^2$.

**The vibrational constants for the upper states.** From the data in Table 2, using the same procedure as was used in determining the lower-state constants, we obtain

$$G' = 342._1\,(v+\tfrac{1}{2}) - 4.6_5\,(v+\tfrac{1}{2})^2,$$

and from Table 4,

$$G' = 335._5\,(v+\tfrac{1}{2}) - 4.5_8\,(v+\tfrac{1}{2})^2.$$

**The values of $\nu_e$.** The values of $\nu_e$ are determined most accurately from the appropriate heads of the 0, 0 bands by correction for the zero-point energies. We obtain $\nu_e$ (I) $= 29499._8$, $\nu_e$ (II) $= 28586._7$ cm$^{-1}$. If the $^2\Pi$ separation is taken to be 975.0 cm$^{-1}$, the values of $\nu_e$ relative to $\nu_e$ of $^2\Pi_{1/2} = 0$ become $29561._7$ and $29499._8$ cm$^{-1}$ — the separation between the two sub-levels being $61._9$ cm$^{-1}$.

**Comparison of GeCl with SnCl.** The superficial similarity between the ultraviolet spectra of GeCl and SnCl has been mentioned. It is of interest to compare the results for the two molecules in more detail. This is done in Table 7. The following points may be noted:

(1) The positions of the levels and the generals trends of the constants are closely similar for the two molecules.
(2) The multiplet state of SnCl at 29000 cm$^{-1}$ has been classed as $^2\Delta$: the separation in the corresponding state of GeCl, 62 cm$^{-1}$, is of the order expected from the separation of 274 cm$^{-1}$ observed for the $^2\Delta$ state in SnCl.
(3) The force-constant in the new upper state of GeCl is about 69 % of that for the ground state: likewise the force-constant in the $^2\Delta$ state of SnCl is about 72 % of that in the ground state.

*Table 7.*

| | GeCl | | | | SnCl | | | |
|---|---|---|---|---|---|---|---|---|
| | $\nu_e$ | $\omega_e$ | $x_e\omega_e$ | *D*, e. v. | $\nu_e$ | $\omega_e$ | $x_e\omega_e$ | *D*, e. v. |
| $^2\Sigma$ | 33992.2 | 526.6 | 0.3 | — | 33582.6 | 432.5 | 1.2 | — |
| $^2\Delta$ | 29561.7 | 335.5 | 4.58 | 4.42 | 28966.3 | 301.6 | 4.1 | 4.28 |
| | 29499.8 | 342.1 | 4.65 | 4.43 | 28692.1 | 300.4 | 4.2 | 4.23 |
| $^2\Pi$ | 975.0 | 405.5 | 1.23 | 4.26 | 2360 | 354.5 | 1.0 | 4.18 |
| | 0 | 407.6 | 1.36 | 3.79 | 0 | 352.6 | 1.2 | 3.21 |
| $k\,(^2\Sigma)/k\,(^2\Pi)$ | 1.68 | | | | 1.50 | | | |
| $k\,(^2\Delta)/k\,(^2\Pi)$ | 0.69 | | | | 0.72 | | | |

(4) The vibrational intervals in both first excited states converge rapidly, so that energies of dissociation can be estimated by the Birge-Sponer extrapolation. For GeCl we obtain $0.7_7$ e. v. and for SnCl $0.6_8$ e. v. The values of $D + \nu_e$ are given in the table: from them dissociation limits may be fixed for GeCl at about 4.3 e. v. and SnCl at about 4.2 e. v. It will also be seen that there is some — but scarcely conclusive — evidence that the ground states dissociate to limits close to these values.

On grounds of the general similarity between SnCl and GeCl, we conclude that the electronic term for the new state is the same as that for the 29000 $\text{cm}^{-1}$ state of SnCl, probably $^2\Delta$. For the same reason, it is to be expected that GeCl should possess a more stable excited state at about 44000 $\text{cm}^{-1}$, corresponding to that found by FOWLER for SnCl[5].

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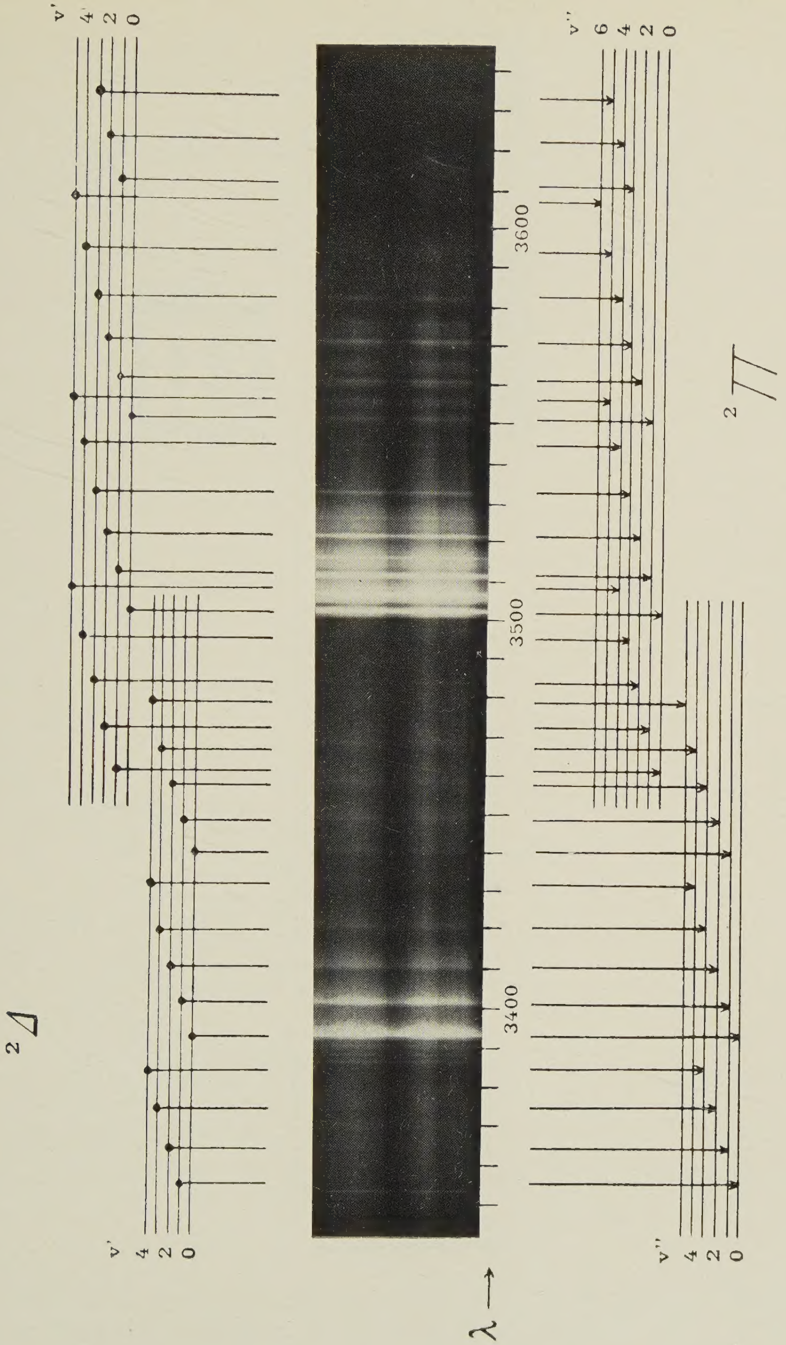

The $^2\Delta - {}^2\Pi$ band-system of GeCl.